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Research Progress and Comparison of Methods for Testing Self Ignition Materials

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Abstract

Fires due to spontaneous combustion make up a very small portion of total fires, but they result in great loss and it's hard to conduct a fire cause identification. This paper is mainly about the research progress of self ignition materials, introduces the methods studying on self ignition materials, including thermal analysis, mathematical formulation and other two new methods: Accelerating Rate Calorimeter and Spontaneous Ignition Tester.

Keyword: spontaneous combustion; wire mesh cube test; mathematical formulation; SIT

1. Introduction

Self ignition (Spontaneous combustion) is defined as combustion caused by heat released by chemical or biological reaction, without an external ignition source. Researches on self ignition are focused on studying the material's tendency to self ignition.

As the heat generated by exothermic reaction won't dissipate in time, the combustion occurs at the place where oxygen exists. The sequences of self ignition go as follows [1]: First, the material must exhibit self heating. Second, self heating must reach a critical condition (a high temperature must be reached rapidly). Third, a sustained smoldering starts. Fourth, the sustained smoldering reaches the outside of the material then erupts into flaming.

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self heating must reach a critical condition (a high temperature must be reached rapidly). Third, a sustained smoldering starts. Fourth, the sustained smoldering reaches the outside of the material then erupts into flaming.

The word self-heating shares similarities with self ignition as well as differences, which could be regarded as a part of self ignition. Self-heating describes the steps that took place before the combustion occurs.

In the presence of biological reaction, it's extremely complex. That is, the heat released from metabolic processes promotes the growth of the microorganisms. At high enough temperature, above the apt temperature range, the heat release will gradually ceased as the microorganisms dying. The upper limit usually is 75℃[2], as the humidity varies. Although at this temperature most materials will not spontaneously combustion, the chemical reaction will be accelerated due to the increase of ambient temperature. [3]

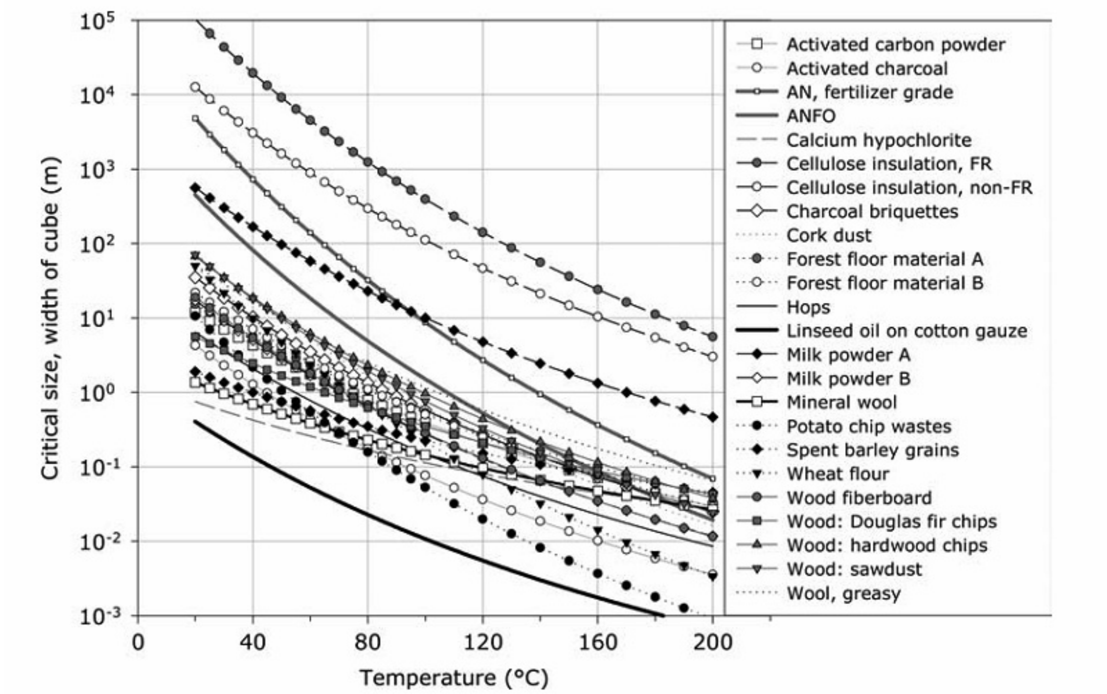

Fig. 1. Relationship between size and critical ambient temperature estimated for various substances by applying a theoretical relationship to small scale laboratory test results

Porosity: Porosity is the ratio of the volume of pores in particles and the total volume. The higher the porosity the larger the surface the particle offers to oxygen molecules to react. Therefore, particles with high porosity ignite more readily than those with low porosity.

2. Summary of Study Method

The main methods that study on self ignition are experimental thermal analysis and mathematical formulation. Experimental thermal analysis involves a large array of calorimetric methods, which usually has a small sample size and used for unknown samples. Mathematical formulation involves small scale experiments at various radiuses, then several self ignition theories could be applied and we can gain the data in real situation though extrapolation of results.

2.1. Thermal Analysis Method

2.1.1 Thermogravimetry (TG) [7]

In thermo gravimetric (TG) analysis the weight of the samples is measured as a function of their temperatures. The first differential equation of TG curve subscribes the amount of heat absorbed and evolved, which is differential thermal analysis (DTA). Figure2 shows a TG and DTG test curve with the characteristic points marked on it. The maximum weight loss temperature (MLT) is an indication of the reactivity of the product and represents the yield of volatile matter produced by pyrolysis. IW is the increase in weight at the beginning of the heating process, which shows the capability of oxygen adsorption during initial heating and the initial oxidation of the sample. Combustion induction temperature (IT) is the temperature of combustion onset.

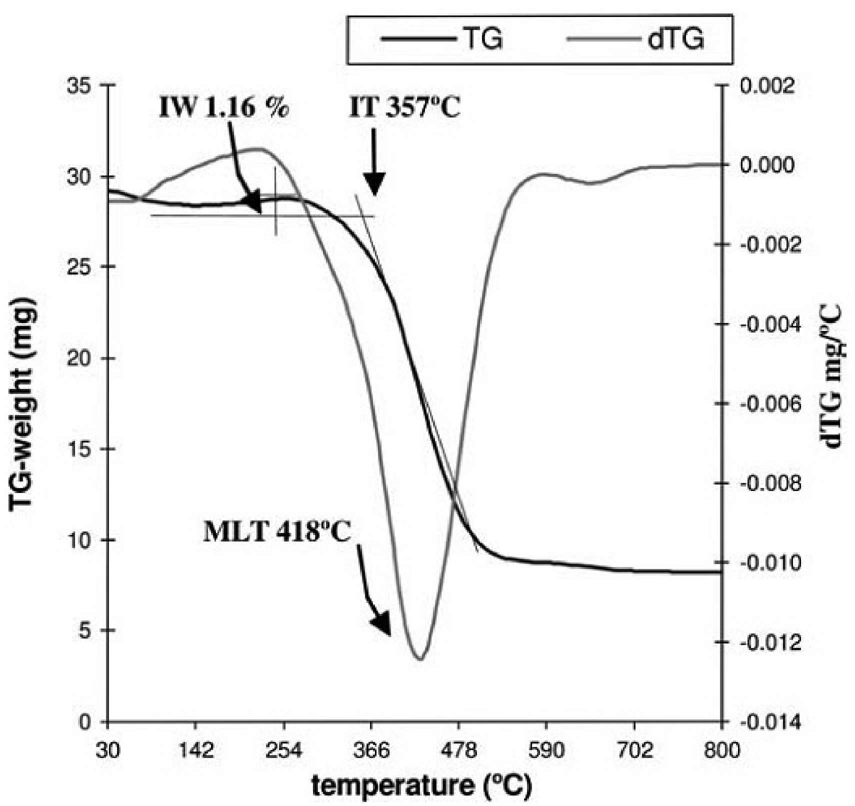

Figure.2.Thermogravimetry results.

Activation energy (Ea) is calculated at the point of maximum weight loss using the data from the TG curve and the equation below. The Ea value has been particularly used for coals from diverse ranks and origins, showing different self combustion risks. [8]

$$\ln\left(\frac{1}{w} \cdot \frac{\mathrm{d}w}{\mathrm{d}t} \right) = \ln A \quad \frac{E_a}{RT}$$

Where w is the weight of unburned combustible, dw/dt the instantaneous rate of weight loss, A the frequency factor, Ea the activation energy, R the universal gas constant and T the absolute temperature.

2.1.2 Differential Scanning Calorimeter(DSC)[9]

The sample is placed in a crucible and heated at a regular rate, previously established. The difference in temperature between that of the sample and that of a reference is measured and recorded against the temperature of the oven so that the exchanges of heat in the sample may be determined. Figure.3 shows the result of a DSC analysis. Initial temperature (IET) is the minimum temperature at which the exothermic reaction begins. Final temperature (FET) is the maximum temperature reached during the exothermic reaction. Change of slope temperature (CST) is the temperature at which the fast exothermic reaction commences, which reflects the tendency to self ignition. The lower CST is the easier to self ignition.

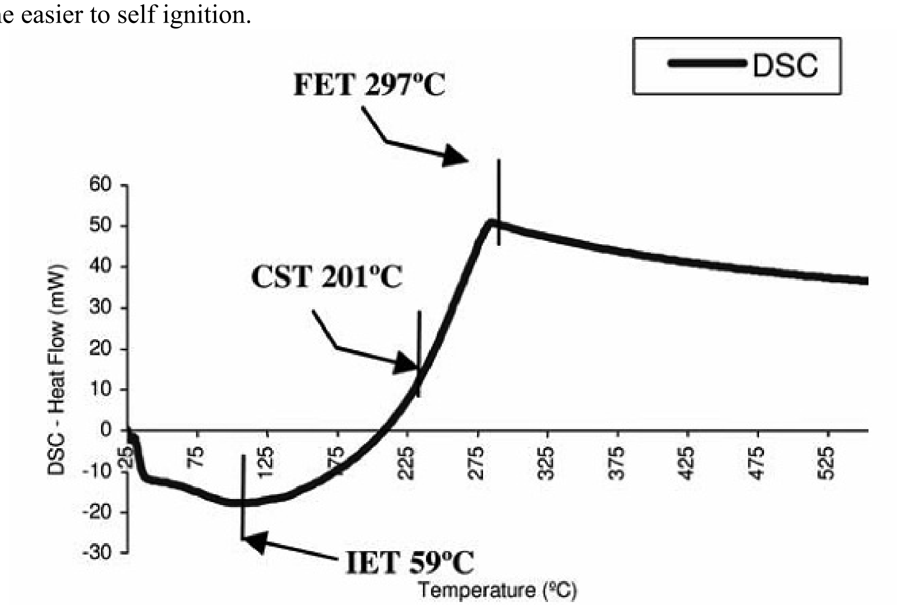

Figure.3 DSC results.

2.1.3 Wire Mesh Cube Test

Wire mesh cube test is developed by Beever[10]. wire basket cubes of various sizes are used, along with an isothermal oven which reproduces environmental temperatures. A sample is held in the oven at a fixed temperature and the evolution in the sample temperature is observed through the time. Three different behaviours can be observed.

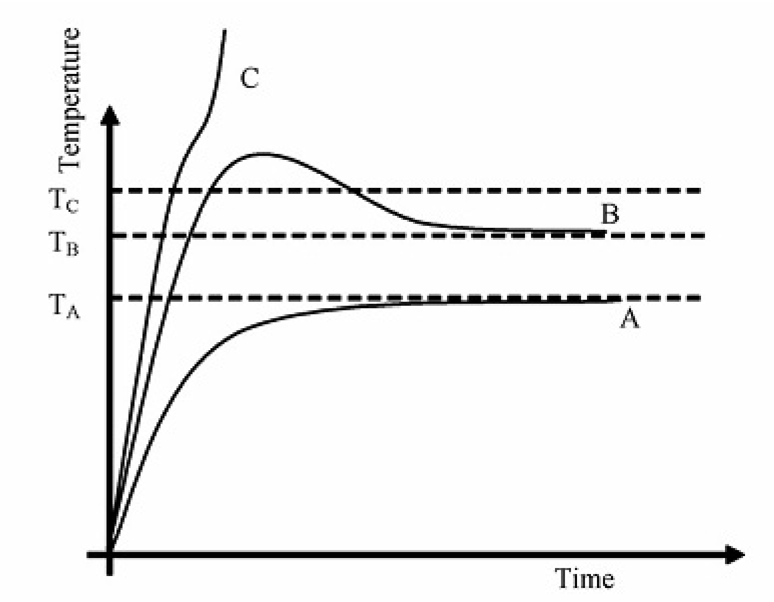

Figure.4 Thermal behaviors (Subcritical, critical and supercritical)

Curve A: subcritical. The sample temperature approaches the oven temperature, but below always it. The sample does not produce heat by itself, no ignition is observed.

Curve B: critical. The sample temperature exceeds the oven temperature for a while and then declines, finally trends to the oven temperature.

Curve C: supercritical. The sample temperature exceeds the oven temperature rapidly and never falls. Eventually, a non-stationary condition is reached, ignition is obtained.

The temperature of the oven is increased in 5 K until the supercritical condition occurs. The temperature of self ignition is the mean between the last critical and the first supercritical temperatures. The test is repeated for different volumes of the sample.

$$\mathrm{SIT} = \frac{(T_B + T_C)}{2}$$

Wire mesh cube test method has been used to identify the self-heating material by United Nations Economic Commission for Europe.[11]

2.1.4 Other Methods

The principle of measurement of C80 calorimetric is similar to DSC, they both were used to obtain the primary heat generation of samples. But C80 can manage much larger amount of sample mass than DSC. DSC has been replaced by C80 in the recent researches. [12]

TAM thermometric is one of the most sensitive thermometry, which has two main functions: well control of isothermal conditions in the water thermostat and effective detection of thermal events. The TAM thermostat is stable to at 0.1mK and a detect limit of 0.05μW can be achieved. Faint reactions can be detected by TAM, such as fermentation, decomposition, slow oxidation, absorption of water.[13]

2.2. Mathematical Formulation Method

The method mentioned above still has the limitation that, because of the relatively small sizes involved, critical temperatures are usually above 100℃, while the real situation may involve normal ambient temperature of 20℃ or so. We need to know what will happen in the real situation, and then we have to formulate the spontaneous combustion. The data gained from the wire mesh cube test can apply to mathematical formulation. [14] By mathematical formulation, not only dimensions of storage leading to ignition can be calculated, but also the required time to reach ignition conditions.

Semenov[15] and Frank-Kamenetskii[16] theories are often impossible to apply in practical situations.

Semenov theory represents the simplest mathematical formulation, where spatial variations of temperature and reaction rate within the body are not considered. Three assumptions for this theory follow:

1.The temperature within the reacting body is spatially uniform.

2.The heat generation is assumed to be due to a single chemical reaction of simple integral order.

3.Both the heat of reaction and activation energy are assumed to be sufficiently large to support ignition behavior.

With these assumptions we can write down two equations that determine the temperature and fuel concentration as functions of time. According to solving the two equations we can get the volume and the required time to reach ignition conditions.

$$C_v \rho V \frac{dT}{dt} = V Q f(c) e^{-E/RT} - S \chi (T - T_a) \quad (1)$$

$$\frac{dc}{dt} = -f(c) e^{-\frac{E}{RT}} \quad (2)$$

where

C_v –heat capacity at constant volume

ρ –density

V –volume

T–temperature of the reacting material (in K)

Ta–ambient temperature of the surroundings (assumed constant in time)

Q–heat of reaction per unit concentration of fuel

f (c) – kinetic rate law

c—concentration of fuel

E—activation energy of the reaction

R—universal gas constant

S—surface area of the interface across which heat is lost to the surroundings

χ —heat transfer coefficient

t—time

Frank-Kamenetskii theory considers temperature gradients within the self-heating body (thereby generalizing Semenov) and often gives better agreement with experiment for solid bodies with low thermal conductivity. Four assumptions for this theory follow:

1.Temperature within the self-heating body varies spatially.

2.The heat generation is assumed to be due to a single chemical reaction of simple integral order.

3.Both the heat of reaction and activation energy are assumed to be sufficiently large to support ignition behavior.

With these assumptions we can write down equation(3) According to solving the equation(3) we can get a critical parameter, by comparing it to the real situation we can judge whether it will reach ignition conditions.

$$k\nabla^2 T + Q f(c) e^{-E/RT} = 0 \qquad (3)$$

T—temperature

Q—heat of reaction per unit concentration of fuel

f (c) — kinetic rate law

c—concentration of fuel

E—activation energy of the reaction

R—universal gas constant

k —heat transfer coefficient

t—time

2.3. The Recent Methods

2.3.1 Accelerating Rate Calorimeter

Accelerating Rate Calorimeter is a kind of adiabatic calorimeter, unlike DSC and C80.ARC has two different measurement modes; heat-wait-search step scanning mode (H-W-S mode) and isothermal scanning mode. ARC is usually used to evaluate the exothermic reaction such as thermal decomposition by the H-W-S mode, and heat accumulation of materials by the isothermal scanning mode. In both mode of ARC, after exothermal with heat generation rate reach above 0.02 K/min, the sample is kept in adiabatic conditions for the duration of the exothermic reaction. In study of spontaneous combustion, ARC was used with H-W-S mode to evaluate the heat accumulation start temperature that means self-heating start temperature in adiabatic condition.

2.4. Spontaneous Ignition Tester

Spontaneous ignition tester was used for measuring materials susceptible to spontaneous ignition under an adiabatic condition, in which heat loss to the surrounding can be reduced to the minimum and any possible heat liberation from exothermal reaction can survive and be used for self-heating. A sample of the substance to be tested is placed at atmospheric pressure under adiabatic conditions and the time taken to reach ignition (adiabatic induction time) is measured. According to thermal ignition theory, it is possible to infer the reaction mechanism by which the sample reaches spontaneous ignition from the change in adiabatic induction time at the set initial temperature. [18-19]

3. Conclusions

The common thermal analysis method (e.g., TG, DSC) are used to obtain relevant information, especially when material of unknown origin and composition is involved. However, wire mesh cube test is more reliable than the common thermal analysis method because volume influence taken into consideration.

The wire mesh cube test method still has the limitation that, because of the relatively small sizes involved, critical temperatures are usually above 100℃, while the real situation may involve normal ambient temperature of 20℃ or so. This means that if the substance has a moisture component, the oven tests will be run with the specimen fully desiccated, while in the real situation, especially organic materials, moisture movements may play a major role.

By mathematical formulation, we can get both the dimensions of storage leading to ignition and the required time to reach ignition conditions, so it is reliable.

Both ARC and SIT has an adiabatic condition, don't need the external heat, so the critical temperature obtained by them usually lower than by the wire mesh cube test.(usually lower than 100℃) [20-22] Water and biological reaction could survive under this condition, and it's suits in the practical situation. The data obtained from these tests is more reliable. However the simple is in a rather small volume in these tests.

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